

(19) Japan Patent Office  
(12) **KOKAI TOKKYO KOHO / JAPANESE UNEXAMINED  
PATENT PUBLICATION (A)**  
(11) Japanese Unexamined Patent Publication No. H2-306902  
(43) Publication date: December 20, 1990

(51) Int. Cl. <sup>5</sup>	ID No.	JPO file No.
A 01 N 25/04	102	7043-4H
25/24		7043-4H
25/30		7043-4H

Request for examination: Not yet made      Number of claims: 1      (Total 11 pages)

---

(54) Title of the invention      Antimicrobial composition

(21) Patent application number: H1-128566

(22) Application date:      May 22, 1989

(72) Inventor      Tadao Kuge  
21-8 Matsubara-cho, Takatsuki-shi  
Osaka-fu

(72) Inventor      Setsuo Tsuruoka  
1-1015, 4-banchi, 3-chome Komatsu  
Higashiyodogawa-ku, Osaka-shi, Osaka-fu

(71) Applicant      Kyowagiken Co., Ltd.  
4-46, 1-chome, Minami-kaneden, Suita-shi  
Osaka-fu

(71) Applicant      Hamari Co., Ltd.  
4-7, 2-chome, Koraibashi, Chuo-ku  
Osaka-shi, Osaka-fu

(74) Agent      Tetsuo Miwa, Patent Attorney

## **Specification**

### **1. Title of the invention**

Antimicrobial composition

### **2. Claims**

What is claimed is:

(1) A water-dispersed antimicrobial composition that consists of an antimicrobial agent, nonionic surfactant, binder and water, wherein the aforesaid nonionic surfactant is a mixture of at least one aromatic nonionic surfactant and at least one non-aromatic nonionic surfactant; the aforesaid binder fixes the antimicrobial agent to the substrate material to be treated; the proportions of the aforesaid antimicrobial agent, nonionic surfactant and binder are,

antimicrobial agent	1-80 wt.%
nonionic surfactant	0.1-8 wt.%
binder	12-99 wt.%;

and the antimicrobial agent is of a type that has been microdispersed to have a mean particle size of 0.2-1  $\mu\text{m}$ .

### **3. Detailed description of the invention**

#### **[Field of industrial application]**

The present invention relates to a water-dispersed antimicrobial composition.

#### **[Background of the invention]**

An antimicrobial agent is a substance that mainly suppresses the growth of, or kills, bacteria, fungi, etc. Suitable antimicrobial agents are selected according to the application and used, for instance, as antimicrobial and anti-odor agents for textile yarns and textile products prepared by spinning such yarns; antibacterial/antifungal agents for paper products, non-woven fabrics, etc.; antibacterial/antifungal paints; antibacterial/antifungal agents for covers made of textiles and toiletry items like toilet seats; and antibacterial/antifungal agents for tiles, floor boards and plastic products like wallpaper, etc.

These antimicrobial agents are not soluble in water. So, they are either blended in a solid form with the substrate material or used as a solution in an organic solvent.

#### **[Problems to be solved by the invention]**

Organic solvents have the problems of toxicity and flammability. Therefore, if the antimicrobial agent is to be used by dissolving in an organic solvent, measures are required with regard to safety and accident prevention. Thus, they lack the so-called "ease in use."

Besides, these antimicrobial agents generally have a particle size of 10-1000  $\mu\text{m}$ . If these need to be blended with the substrate, it is difficult to make them into finer particles, a lot of time and cost are involved, and there is a limit to which the particles can be made small. Moreover, they have other problems like the need to be added at a high concentration to sustain their useful effect when used by blending with the substrate, because they get dispersed all over the substrate.

[Means for solving the problems]

The present inventors undertook painstaking investigations to solve the above-mentioned problems that arise in the use of aforesaid types antimicrobial agents and, as a result, found out that the antimicrobial agent could be microdispersed to a mean particle size of 0.2 to 1  $\mu\text{m}$  if it is dispersed in water along with at least one aromatic nonionic surfactant and at least one non-aromatic nonionic surfactant, the dispersed state of the particles was not disturbed if a binder that can firmly fix the antimicrobial agent to the substrate was added to the aqueous dispersion of the aforesaid antimicrobial agent at a certain proportion, the various problems associated with the use of organic solvents and the problems that arose when the antimicrobial agent was blended in the form of a solid could be solved, the composition prepared was safe and easy to use, the composition could be used efficiently as the antimicrobial agent got fixed firmly to the substrate, and moreover the water-dispersed antimicrobial composition could be prepared at a low cost in this manner. These findings led to the present invention.

In short, the present invention relates to a water-dispersed antimicrobial composition, consisting of an antimicrobial agent, a nonionic surfactant that is a mixture of at least one aromatic nonionic surfactant and at least one non-aromatic nonionic surfactant, a binder and water, wherein the proportions of the aforesaid antimicrobial agent, nonionic surfactant and binder are 1-80% (wt.%, hereinafter also) antimicrobial agent, 0.1-8% nonionic surfactant and 12-99% binder, and the antimicrobial agent is microdispersed in the form of particles of mean particle size of 0.2-1  $\mu\text{m}$ .

In the present invention, methyl 2-benzimidazolyl carbamate, 2,4,5,6-tetrachloro isophthalonitrile-N-(fluorodichloromethylthio)phthalimide,  $\alpha$ -bromocinnamaldehyde, zinc omadine, N,N-dimethyl-N'-phenylsulfamide, bis(dimethylthiocarbamoyl)disulfide, 5-chloro-2-methyl-4-isothiazoline-3-one, 2-methyl-4-isothiazoline-3-one, thiabendazole, chlorhexidine hydrochloride, triclocarban, 3-trifluoromethyl-4,4'-dichlorocarbanilide, clotrimazole, tolnaftate, etc., are used singly or in combinations of two or more as the antimicrobial agent.

In the present invention, the nonionic surfactant is a mixture of at least one aromatic nonionic surfactant and at least one non-aromatic nonionic surfactant.

The reason for using the nonionic surfactant is that this type of surfactant does not have reactivity with the antimicrobial agent. The reason for using a mixture of an aromatic nonionic surfactant and a non-aromatic nonionic surfactant is to microdisperse the antimicrobial agent to a mean particle size of 0.2-1  $\mu\text{m}$ . In other words, the antimicrobial agent cannot be

microdispersed to a mean particle size of 0.2-1  $\mu\text{m}$  as it gets aggregated and does not become microdispersed in water unless such a mixture of nonionic surfactants is used.

The exact reason why the antimicrobial agent gets microdispersed to a mean particle size of 0.2-1  $\mu\text{m}$  only when a mixture of aromatic nonionic surfactant and non-aromatic nonionic surfactants is used is not well-understood at present. However, one reason for this could be that the aromatic nonionic surfactant has miscibility with the antimicrobial agent. But when the aromatic nonionic surfactant alone is used, the results are not very good, probably because of its very high miscibility with the antimicrobial agent, and an aqueous dispersion in which the antimicrobial agent is microdispersed cannot be obtained.

In the present invention, a polyoxyethylene alkylphenyl ether, polyoxyethylene diphenyl ether, polyoxyethylene naphthyl ether, etc. may be used, for instance, as the aromatic nonionic surfactant.

Practical examples of such aromatic nonionic surfactants are polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene diphenyl ether, polyoxyethylene naphthyl ether, etc.

On the other hand, polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, polyhydric alcohol fatty acid ester, polyoxyethylene polyhydric alcohol fatty acid ester, sucrose fatty acid ester, polyoxyethylene fatty acid amide, polyoxyethylene alkylamine, polyoxyethylene glycerol fatty acid ester etc. are used, for instance, as the non-aromatic nonionic surfactant.

Practical examples of such non-aromatic nonionic surfactants are polyoxyethylene lauryl ether, polyoxyethylene oleyl ether, polyoxyethylene tridecyl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene laurate, polyoxyethylene oleate, polyoxyethylene stearate, polyoxyethylene laurylamine, sorbitan laurate, sorbitan palmitate, sorbitan stearate, sorbitan oleate, polyoxyethylene sorbitan laurate, polyoxyethylene sorbitan palmitate, polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan oleate, ethylene oxide-propylene oxide block polymer, polyoxyethylene polyoxypropylene lauryl ether, polyoxyethylene polyoxypropylene oleyl ether, etc.

It is preferable to use the aromatic nonionic surfactant and non-aromatic nonionic surfactant at a weight ratio of 1:4 to 4:1.

In the present invention, a binder is used for firmly fixing the antimicrobial agent to the substrate. Phenol resin, olefin resin, isocyanate resin, epoxy resin, vinyl acetate resin, acrylic copolymer resin, cyanoacrylic resin, urethane resin, nitrile rubber, SBR resin, and ethylene resin, for instance, are used in the form of water emulsions singly or in combinations of two or more as the binder.

Practical examples of such binders are polyvinyl acetate, polyvinyl butyral, polyacrylate ester, acrylic vinyl copolymer, polyethylene, ethylene-vinyl acetate copolymer, polyvinyl chloride-vinyl acetate copolymer, nylon, polyethylene terephthalate, polybutylene terephthalate, urea-formaldehyde condensate, resorcinol-formaldehyde condensate, epoxy resin, polyurethane, vinyl urethane, polyisoprene, polychloroprene, acrylonitrile-butadiene copolymer, styrene-

butadiene copolymer, styrene-butadiene-vinyl pyridine terpolymer, polyisobutylene, butyl rubber, polyimide, etc.

In the present invention, the proportions of the antimicrobial agent, nonionic surfactant and the binder are 1-80% antimicrobial agent, 0.1-8% nonionic surfactant and 12-99% binder, all in terms of the solid components.

In other words, when the proportion of the antimicrobial agent is less than what is specified above, its antimicrobial action would not be sufficiently manifested, and if it is more than the above-specified range, it becomes impossible to microdisperse the antimicrobial agent into fine particles. Besides, the proportion of binder would be reduced, and as a result the antimicrobial agent cannot be fixed to the substrate firmly.

When the proportion of the nonionic surfactant is less than the above-specified range, the antimicrobial agent cannot be microdispersed into fine particles. On the other hand, if it exceeds the above-specified range, the nonionic surfactant tends to aggregate and it becomes impossible to microdisperse the antimicrobial agent into fine particles.

When the proportion of the binder is less than what is specified above, the antimicrobial agent cannot be fixed firmly to the substrate, and if it exceeds the above-specified range, the composition would become tacky and would not form a good water-dispersion. Besides, when such a composition is used to treat textile products and similar materials, the feel of the treated products would not be good.

The particularly preferable proportions of the antimicrobial agent, nonionic surfactant and the binder in the composition are 5-60% of antimicrobial agent, 0.5-6% of the nonionic surfactant and 34-94.5% of binder.

Water is an essential component in the present invention. As long as the aforesaid composition of nonaqueous component comprising the antimicrobial agent, nonionic surfactant and binder is maintained in the above-mentioned range, water can be added over a wide range and a microdispersed aqueous dispersion can still be maintained. For example, the microdispersed water-dispersion can be prepared by adding water over the wide range of 100 to 1 million parts by weight for 100 parts by weight of the afore-mentioned nonaqueous component comprising the antimicrobial agent, nonionic surfactant and binder. Thus, the amount of water added can vary over a wide range. In the present invention, if we try to specify the proportions of the four essential components, i.e., the antimicrobial agent, nonionic surfactant, binder and water, the proportion of the nonaqueous components would vary widely depending on the amount of water used. To avoid this, the composition is specified only for the 3 components, i.e., the antimicrobial agent, the nonionic surfactant and the binder.

At the time of its production, the aforesaid antimicrobial composition is normally prepared as an aqueous dispersion having 5-50% of the nonaqueous component consisting of the antimicrobial agent, nonionic surfactant and binder, and it is diluted with water to a suitable concentration at the time of its use according to the application.

The antimicrobial composition of the present invention can contain small amounts of additional components like antifoaming agents, in addition to the aforesaid four components, i.e., the antimicrobial agent, nonionic surfactant, binder and water.

The antimicrobial composition of the present invention can be used, for instance, as an antimicrobial/anti-odor agent for textile yarns and products prepared by spinning such yarns; antibacterial/antifungal agents for paper products, non-woven fabrics, etc.; antibacterial/antifungal; antibacterial/antifungal agents for covers made of textiles, toiletry items like toilet seats; and antibacterial/antifungal agents for tiles, flooring boards and plastic products like wallpaper, etc.

For using on the aforesaid items, the composition of the present invention may be applied or spray-painted on the surface of the substrate or the item may be dipped in the antimicrobial composition (or its water-diluted dispersion). However, when using with paint, it is mixed with the paint.

#### [Embodiments]

The present invention is explained below in greater detail, citing some practical examples of applying it. Before explaining the examples in details, it should be mentioned that the effect of the mean particle size of the antimicrobial agent on its content in the substrate is demonstrated in Experimental example 1, the difference in the content of the antimicrobial agent in the substrate caused by the presence or absence of binder is demonstrated in Experimental example 2, and the difference in mean particle size of the antimicrobial agent and its content in the substrate because of differences in the nonionic surfactant used is shown in Experimental example 3.

#### Experimental example 1

Antimicrobial agent, nonionic surfactant, binder and water were prepared as per the below-listed composition by dispersing in different devices to obtain dispersions with different mean particle size of antimicrobial agent.

##### Antimicrobial agent

Chlorohexidine hydrochloride	15%
------------------------------	-----

Triclocarban	20%
--------------	-----

##### Nonionic surfactant

Polyoxyethylene nonylphenyl ether (HLB 8.9)	2%
---	----

Polyoxyethylene nonylphenyl ether (HLB 11.6)	1%
--	----

Polyoxyethylene lauryl ether (HLB 14.0)	1%
---	----

Polyoxyethylene stearate (HLB 7.7)	1%
------------------------------------	----

Ethylene oxide-propylene oxide block polymer (Mean molecular wt. 1,250,	
---	--

20% ethylene oxide)	1%
---------------------	----

Water	59%
-------	-----

The above-listed antimicrobial agent, nonionic surfactant and water were stirred with an ordinary stirrer to prepare an aqueous dispersion. This aqueous dispersion was then stirred in a grinder mill, ultrasonic stirrer or a continuous sealed horizontal mill to microdisperse the antimicrobial agent. Table 1 shows the types of dispersion device used, duration of dispersion and the mean particle size of the antimicrobial agent. The mean particle size of the antimicrobial agent was measured using a particle analyzer manufactured by Shimadzu Corp.

Table 1

	Mean particle size of antimicrobial agent (μm)			
	Dispersed for 0 minutes	Dispersed for 30 minutes	Dispersed for 60 minutes	Dispersed for 24 hours
Grinder mill	5.5	5.5	5.5	1.8
Ultrasonic stirrer	5.5	5.0	5.0	1.9
Continuous sealed horizontal mill	5.5	0.59	0.48	-

As shown in Table 1, an aqueous dispersion in which the antimicrobial agent is microdispersed in the form of particles can be obtained in a short dispersing time when a continuous sealed horizontal mill is used.

Next, 3 types dispersions containing the afore-mentioned antimicrobial agents were each diluted 90 times with water, swatches of cotton fabric were soaked in each diluted solution for 30 minutes, centrifuged for 2 minutes, dried for 30 minutes at 100°C and then allowed to cool in a desiccator. The cotton fabric was thus treated with the antimicrobial agent.

The content of antimicrobial agent taken in the swatches of cotton fabric thus treated was measured by the absorbance method, and Table 2 shows the relationships among the device used for dispersion, the mean particle size of the antimicrobial agent, its content.

Table 2

	Mean particle size of antimicrobial agent (μm)	Content of antimicrobial agent (ppm)
Grinder mill	1.8	300
Ultrasonic stirrer	1.9	200
Continuous sealed horizontal mill	0.48	2,000

It can be seen from Table 2 that the content of antimicrobial agent in the cotton fabric was much higher when the mean particle size of the antimicrobial agent was small.

#### Experimental example 2

Four types of antimicrobial compositions were prepared, by either adding binder (polyethyl acrylate) at the proportions shown below or without the binder, with each of the two types of dispersion containing antimicrobial agent prepared in Experimental example 1, i.e., the dispersion in which antimicrobial agent of mean particle size 1.8  $\mu\text{m}$  was dispersed and the dispersion in which the antimicrobial agent of mean particle size 0.48  $\mu\text{m}$  was dispersed.

**Binder added**

Dispersion prepared in Experimental example 1	50%
Polyethyl acrylate	25%
Water	25%

**Binder not added**

Dispersion prepared in Experimental example 1	50%
Water	50%

These 4 types of antimicrobial compositions were diluted 15 times with water and then, swatches of cotton fabric were treated by soaking in the diluted antimicrobial compositions and processing as in Experimental example 1.

These treated swatches of cotton fabric were washed following the method of JIS L 0217 103 and changes in the content of antimicrobial agent in the fabric with increased number of washings were examined. The results are shown in Table 3. In Table 3, the antimicrobial compositions are designated by the mean particle size of the antimicrobial agent and whether a binder was used.

Table 3

	Content of antimicrobial agent (ppm)			
	Washed 0 times	Washed 5 times	Washed 10 times	Washed 30 times
Mean particle size 1.8 $\mu\text{m}$ Without binder	2,000	200	0	0
Mean particle size 0.48 $\mu\text{m}$ Without binder	2,000	500	100	100
Mean particle size 1.8 $\mu\text{m}$ With binder	2,000	500	20	0
Mean particle size 0.48 $\mu\text{m}$ With binder	2,000	1,850	1,600	1,600

As shown in Table 3, with the antimicrobial composition having antimicrobial agent of mean particle size 0.48  $\mu\text{m}$  microdispersed and the binder therein, a high content of antimicrobial agent was present even after 30 washings.

#### Experimental example 3

Antimicrobial agent, nonionic surfactant, binder and water at the proportions listed in Table 4 were dispersed for 60 minutes in a continuous sealed horizontal mill to prepare the 3 types of antimicrobial compositions, i.e., samples A, B and C. In Table 4, the values shown against each component are its percent content. It can be seen from Table 4 that the sample compositions A, B and C differed only with respect to the nonionic surfactant used, they being identical with regard to the rest of the components, i.e., the antimicrobial agent, binder and water.

Table 4

	Antimicrobial compositions		
	Sample A	Sample B	Sample C
Antimicrobial agent			
Chlorohexidine hydrochloride	7.5	7.5	7.5
Triclocarban	10.0	10.0	10.0
Nonionic surfactant			
Polyoxyethylene nonylphenyl ether (HLB 8.9)	1.0	2.0	-
Polyoxyethylene nonylphenyl ether (HLB 11.6)	0.5	1.0	-
Polyoxyethylene lauryl ether (HLB 14.0)	0.5	-	1.0
Polyoxyethylene stearate (HLB 7.7)	0.5	-	1.0
Ethylene oxide-propylene oxide block polymer (Mean molecular wt. 1,250, 20% ethylene oxide)	0.5	-	1.0
Binder			
Polyethyl acrylate	25.0	25.0	25.0
Water	54.5	54.5	54.5

Table 5 gives the measured values of mean particle size of the antimicrobial agent in the antimicrobial composition samples A, B and C thus obtained.

The above antimicrobial compositions A, B and C were diluted 30 times with water, swatches of cotton fabric treated by immersing in the diluted compositions and processing as in Experimental example 1.

These treated swatches of cotton fabric were washed following the method of JIS L 0217 103 and changes in the content of antimicrobial agent in the fabric with increased number of washings were examined. The results are shown in Table 5.

Table 5

Sample	Mean particle size of antimicrobial agent ( $\mu\text{m}$ )	Content of antimicrobial agent (ppm)			
		Washed 0 times	Washed 5 times	Washed 10 times	Washed 30 times
A	0.48	2,000	1,850	1,600	1,600
B	2.5	2,000	400	100	0
C	2.8	2,000	200	0	0

In the antimicrobial composition Sample A, a 1:1 weight ratio mixture of the aromatic nonionic surfactant (polyoxyethylene nonylphenyl ether) and the non-aromatic nonionic surfactants (polyoxyethylene lauryl ether, polyoxyethylene stearate and ethylene oxide-propylene oxide block polymer) is used. In Sample A, the antimicrobial agent was microdispersed at mean particle size 0.48  $\mu\text{m}$ , as shown in Table 5, and the antimicrobial agent remained at the high content of 1,600ppm even after the fabric was washed 30 times.

Contrary to this, in the antimicrobial composition Sample B in which only aromatic nonionic surfactants were used, the mean particle size of the antimicrobial agent was 2.5  $\mu\text{m}$  and it was not in the form of fine particles as in Sample A. After 30 washings, the content of the antimicrobial agent in this sample became 0. In the antimicrobial composition Sample C where only non-aromatic nonionic surfactants were used, the mean particle size of the antimicrobial agent was 2.8  $\mu\text{m}$  and it was not in the form of fine particles as in sample A. After 30 washings, the content of the antimicrobial agent became 0.

#### Example 1

Antimicrobial agent, nonionic surfactant, binder and water were dispersed as per the below-listed composition by blending in a continuous sealed horizontal mill for 60 minutes and a water-dispersed antimicrobial composition in which antimicrobial agent particles of mean particle size 0.48  $\mu\text{m}$  were microdispersed was prepared.

#### Antimicrobial agent

Chlorohexidine hydrochloride

10%

Triclocarban	2%
Tolnaftate	1%
<b>Nonionic surfactant</b>	
Polyoxyethylene nonylphenyl ether (HLB 8.9)	1%
Polyoxyethylene lauryl ether (HLB 14.0)	0.3%
Polyoxyethylene sorbitan monooleate (HLB 15.0)	0.2%
<b>Binder</b>	
Methylmethacrylate-hydroxyethylene methacrylate copolymer (copolymerization ratio 90:10)	16%
Ethylene-vinyl acetate copolymer (copolymerization ratio 50:50)	16%
Water	53.5%

In the above composition, the proportion of the nonaqueous components, i.e., the antimicrobial agents, nonionic surfactants and binders, is as follows.

Antimicrobial agents	28.0%
Nonionic surfactants	3.2%
Binders	68.8%

The amount of water was about 115 parts by weight for 100 parts by weight of nonaqueous components. The weight ratio of the aromatic (polyoxyethylene nonylphenyl ether) and non-aromatic (polyoxyethylene lauryl ether and polyoxyethylene sorbitan monooleate) nonionic surfactants was 2:1.

Next, the aforementioned antimicrobial composition of Example 1 was diluted 30 times with water. Swatches of cotton fabric were treated with the antimicrobial agent by soaking in the diluted antimicrobial composition for 30 minutes at room temperature, centrifuging for 2 minutes, drying for 30 minutes at 100°C and then allowing them to cool in a desiccator. The changes in the content of antimicrobial agent with increase in the number of washings and the antimicrobial and anti-odor properties of the swatches of treated cotton fabric thus obtained were measured.

[Changes in the content of antimicrobial agent with increase in the number of washings]

The aforementioned treated swatches of cotton fabric were washed following the method of JIS L 0217 103 and changes in the content of antimicrobial agent in the fabric with increased number of washings were examined. The results are shown in Table 6.

Table 6

No. of washings	Content of antimicrobial agent in the cotton fabric
0	7,000 ppm
5	6,000 ppm
10	5,000 ppm
30	5,000 ppm

As shown in Table 6, the fabric treated with antimicrobial composition of Example 1 had as high as 5,000 ppm of antimicrobial agent even after 30 washings.

[Antimicrobial and anti-odor property]

The aforementioned treated cotton fabric swatches were tested for reduction in microbial count by the Test Method 100 of AATCC (American Association of Textile Chemists and Colorists) to examine the antimicrobial and anti-odor property. The challenge organism was *Staphylococcus aureus* IFO 13277.

The difference between the aforementioned treated and 30 times washed cotton fabric swatches and the untreated cotton fabric in the change in the bacterial count was 5.103, well above the reference value of 1.6 (the value at which the treated material is considered to have suppressing action on the growth of the challenge organism). Thus, the treated fabric showed sufficient suppressive effect on bacterial growth.

Next, the aforementioned antimicrobial composition of Example 1 was diluted 30 times with water. Swatches of acrylic fabric were treated with the antimicrobial agent by soaking in the diluted antimicrobial composition for 30 minutes at room temperature, centrifuging for 2 minutes, drying for 30 minutes at 100°C and then allowing them to cool in a desiccator. The changes in the content of antimicrobial agent with increase in the number of washings and the antimicrobial and anti-odor properties of the swatches of the treated acrylic fabric (Sample 1) were measured.

Aside from this, the aforementioned antibacterial composition of Example 1 was diluted 100 times with water; swatches of acrylic fabric were soaked at room temperature in the diluted antimicrobial composition and processed as above to prepare acrylic fabric samples with less initial concentration of antimicrobial agent (Sample 2). The changes in the content of antimicrobial agent with increase in the number of washings and the antimicrobial and anti-odor properties of the treated acrylic fabric were measured.

[Changes in the content of antimicrobial agent with increase in the number of washings]

The aforesaid acrylic fabric samples 1 and 2 were washed following the method of JIS L 0217 103 and changes in the content of antimicrobial agent in the fabric with increased number of washings were examined. The results are shown in Table 7. This testing was carried out keeping in mind the use of acrylic fabric in panty stockings. Therefore, the number of washings was kept at 5, considering the washings required in this application.

Table 7

	Content of antimicrobial agent (ppm)	
	Washed 0 times	Washed 5 times
Sample 1	6,490	5,900
Sample 2	1,800	1,500

As shown in Table 7, even in the Sample 2 which had a low initial content of antimicrobial agent, the high antimicrobial content of 1,500ppm was recorded after 5 washings.

[Antimicrobial and anti-odor property]

The aforementioned treated acrylic fabric samples 1 and 2 were tested for reduction in microbial count by the Test Method 100 of AATCC to examine the antimicrobial and anti-odor property.

The challenge organism used for the test was *Staphylococcus aureus* IFO 13277 as with the earlier-mentioned cotton fabric.

The difference in the change in the number of the bacteria used in the test between the aforementioned acrylic fabric samples 1 and 2 after 5 washings and in the untreated acrylic fabric was more than the reference value of 1.6, as shown in Table 8 given below.

Table 8

	Difference in change of bacterial count
Sample 1	5.205
Sample 2	5.110

Example 2

Antimicrobial agent, nonionic surfactant, binder and water were dispersed as per the below-listed composition as in Example 1 to prepare a water-dispersed antimicrobial composition in which antimicrobial agent particles of mean particle size 0.59  $\mu\text{m}$  were microdispersed. Here, in the solid state, the antimicrobial agent had a mean particle size of 30  $\mu\text{m}$ .

Antimicrobial agent

Methyl 2-benzimidazolyl carbamate 15%

Nonionic surfactant

Polyoxyethylene nonylphenyl ether (HLB 8.9) 1%

Polyoxyethylene sorbitan monooleate (HLB 15.0) 2%

Binder	
Polyethyl acrylate	15%
Styrene-butadiene copolymer (copolymerization ratio 25:75)	8%
Water	59%

In the above composition, the proportion of the nonaqueous components, i.e., the antimicrobial agent, nonionic surfactants and binder, is as follows.

Antimicrobial agent	36.6%
Nonionic surfactants	7.3%
Binder	56.1%

The amount of water was about 144 parts by weight for 100 parts by weight of nonaqueous components. The weight ratio of the aromatic (polyoxyethylene nonylphenyl ether) and non-aromatic (polyoxyethylene sorbitan monooleate) nonionic surfactants was 1:2.

Next, the antimicrobial composition was diluted 10 times with water. This fluid was uniformly spray-painted on the surface of a polyvinyl chloride sheet (50 x 50cm) and dried to prepare a surface-active antimicrobial polyvinyl chloride sheet.

A piece of this sheet was chopped finely; the antimicrobial agent extracted with methanol and its content was determined by the method of absorbance. The content of antimicrobial agent was 0.05%.

#### Comparison example 1

Methyl 2-bezoimidazolyl carbamate of mean particle size 30  $\mu\text{m}$  was added to a vinyl chloride resin to the extent of 0.2% of the resin and made into a sheet after kneading the mixture. A part of this sheet was finely chopped and the content of antimicrobial agent determined as in Example 2. Its content was 0.19%.

Water-resistance test and fungal resistance test were carried out with the sheets prepared in the above Example 2 and this Comparison example 1. The results are given in Table 9.

#### [Water resistance test]

50 g each of the sheets of the above Example 2 and Comparison example 1 were soaked in water, placed under running water for 30 days, dried and used as test samples.

1 g was taken from each sample, chopped finely, the antimicrobial agent was extracted with methanol, and its content measured by the absorbance method. The results of these measurements were compared with the content of the antimicrobial agent in the samples before the water resistance test. The results are shown in Table 9 given later.

[Fungal resistance test]

28 mm diameter circular specimens were taken from the sheets before and after the water resistance test. These were then pasted on the surface of a flat medium for paint as specified in JIS Z 2911 1981.7.4. 1 ml of spore suspension was sprayed on the surface of this specimen and also directly on the surface of a medium and cultured for 30 days at 27 °C. The fungus resistance was then measured. Three replicate samples were used in each test. The results of this test are given in Table 9. In Table 9, the 3 replicate samples are referred to as (a), (b) and (c).

Table 9

Sample	Content of anti-microbial agent (%)	Fungal resistance*		
		(a)	(b)	(c)
Pre-water resistance test sample of Example 2	0.05	3	3	3
Post-water resistance test sample of Example 2	0.04	3	3	3
Pre-water resistance test sample of Comparison example 1	0.19	3	3	3
Post-water resistance test sample of Comparison example 1	0.09	1	2	1

Note: \* Fungal resistance criteria

3. No hyphal growth seen on the inoculated part of the test sample
2. The area under hyphal growth seen on the inoculated part of the sample did not exceed 1/3<sup>rd</sup> of the total area.
1. The area under hyphal growth seen on the inoculated part of the sample was more than 1/3<sup>rd</sup> of the total area.

As shown in Table 9, in the sheet prepared in Example 2 of the present invention, there was not much reduction of the content of antimicrobial agent in the water-resistance test. Even after the water resistance test, the material showed very good fungal resistance in the fungal resistance test. Contrary to this, in the material prepared in Comparison example 1, there was significant reduction of the content of antimicrobial agent in the water-resistance test and the fungal resistance of the material was inferior in comparison to Example 2 in the fungal resistance test after the water resistance test. Although the content of antimicrobial agent post-water resistance test was higher in Comparison example 1 than in Example 2, it had poorer fungal resistance. This was because the antimicrobial composition was applied on the surface of the material by spray-painting in Example 2 and therefore, the antimicrobial agent was present at the surface in a concentrated fashion. Thus, although the overall content of antimicrobial agent was not very high, it showed superior fungal resistance. In Comparison example 1, on the other hand, the antimicrobial agent was blended with the material and the amount of antimicrobial agent on the surface layer was not much relative to its total content. This is

believed to be the reason why this material's fungal resistance post-water resistance test was poorer.

**[Advantageous effect of the invention]**

As explained above, the present invention is capable of providing an antimicrobial composition in the form of an aqueous dispersion, which is safe and easy to use, the antimicrobial agent of which gets firmly fixed to the substrate giving it excellent antimicrobial and anti-odor properties and fungal resistance, and which can therefore be used efficiently.

Applicant: Kyowagiken Co., Ltd.; and 1 other company

Agent: Tetsuo Miwa, Patent attorney